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The use of leaching tests to assess metal release from contaminated marine sediment under CO_2 leakages from CCS

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Abstract

This study provides a better knowledge of key parameters controlling the mobility of Dissolved Organic Carbon (DOC), As, Cd, Cr, Cu, Ni, Pb and Zn from contaminated marine sediment in contact with acidified seawater using static and dynamic standard leaching tests. These procedures have been modified in order to use different leaching agents, L/S ratios, contact times and pH values that simulate seawater acidification under CO_2 leakages scenarios. Studied sediment from a potential area of CO_2 storage, shows a high acid neutralisation capacity ($ANC_{pH=4}$=3.58 eq/kg) for deionised water as well as for seawater ($ANC_{pH=4}$=3.97 eq/kg). The availability control mechanism is shown by releasing Cd with seawater at pH values 6, 7 and 8 and by the releasing of Zn with seawater at pH 6; the solubility control mechanism appears for Ni release using natural seawater. Experimental results of metal release from the pH dependence leaching test are modelled with Visual MINTEQ geochemical software to predict metal release from sediment, obtaining minor differences with experimental values. An improvement in the metal release results has been obtained considering in the model the influence of the DOC, Fe- and Al-(hydr)oxides, humic acids and fulvic acids. The obtained results would be useful as a line of evidence input for the risk assessment of a Carbon Capture and Storage site where acidified seawater at different concentrations of CO_2 is in contact with sediment.

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Keywords: Sediment; metal release; CO_2 leakage; leaching tests.

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1. Introduction

The rapid increase of carbon dioxide (CO_2) levels in the atmosphere is supposed to be the major contributing factor to global climate change associated with global warming and ocean acidification. A possible global warming mitigation proposed at planetary level for this problem is Carbon Capture and Storage (CCS) in geological formations, where sub-seabed geological formations and especially storage in deep saline aquifers is the most promising sequestration method [1, 2]. The dissolution of CO_2 into a fluid phase, directly in the saline aquifer of storage (aqueous brines) or during the CO_2 gas leakage at short or long distances (native pore water, seawater, groundwater) generates acidic CO_2 rich fluids. These fluids can leak in the same way that CO_2 gas (vertical and horizontal diffusion through confining layers and sediment, advection through fractures and faults, contact in bulk). Such leakages can dissolve the cap rock and would be in contact with different formation layers including contaminated sediment cores. As a consequence of this, one of the main risks of CCS in these sites is the mobilisation of some substances from the surrounding environment [3, 4].

Spain, like other countries, has proposed specific areas as potential structures for CO_2 storage [5, 6]. Four of them are located in the continental shelf of the Cantabrian Sea (Northern Spain); in some of these coastal and estuarine areas, sediment presents high concentrations of pollutants [7, 8]. Hence, before developing CCS technology, a complete knowledge of sediment behaviour under different acidification conditions becomes essential.

The potential availability of metals to marine organisms under various environmental situations is extremely useful information in a risk assessment procedure of CCS technology [9]. The evaluation of the release of constituents from solid matrices (sediment, dredged material or waste materials) has been developed by leaching tests simulating a high number of different conditions [10, 11]. The leaching process is very complex and one single test cannot provide a complete understanding of the heavy metal mobility. In order to have a better vision of the leaching process, a variety of tests is used to determine metal release from solid matrices under changing environmental conditions [12].

Leaching tests have been applied previously to study and assess the mechanisms and efficiency of metal release processes from solids in contact with liquid. In this way, different approaches have previously been used to simulate acidification scenarios due to CO_2 leakages from CCS [13-17]. A set of leaching tests developed by the Nederlands Normalisatie-instituut-NEN, (NEN 7341) or the European Committee for Standardization-CEN, through Technical Specifications-TS, (CEN/TS 15364, CEN/TS 14405 and CEN/TS 14429) or European Standards-EN, (EN12457) are commonly used to determine the influence of pH on the release of inorganic constituents from solid materials.

The main objective of the present work is to predict the Dissolved Organic Carbon (DOC), As, Cd, Cr, Cu, Ni, Pb and Zn release from contaminated sediment in contact with acidified deionised water and seawater. In the present work, standardised [18-22] and modified methods are used to simulate scenarios where acidified seawater, at different dissolved CO_2 concentrations, is in contact with contaminated sediment from a potential Spanish CO_2 storage site. Visual MINTEQ geochemical software is proposed to model experimental results of metal release from pH dependence leaching test.

2. Methodology

2.1. Materials

The studied surface sediment comes from an estuarine area, a site reserved as a potential CO_2 store, in the continental shelf of the Cantabrian Sea (northern Spain) [5].This area is characterised by high industrial activity

and by a considerable urban density, therefore, the sediment contains significant concentrations of metals and organic pollutants [7, 23]. Surface sediment (0-5 cm layer) with its initial water content, was collected using a plastic paddle, sieved through 2 mm, homogenised and frozen in plastic bags until use. The main crystalline phase of the sediment under study is quartz with a 57% of the total mass. Aluminium oxide (8%), and calcium oxide (7%), usually as calcite and dolomite are also present. Total Organic Carbon (TOC) is 1.74%. The sediment has high concentrations of Zn and Pb, 4030 and 407 mg/kg respectively, while As, Cd, Cr, Cu and Ni concentrations range from 10 to 60 mg/kg.

When acidified seawater at pH 5, 6 or 7 was needed as a leaching agent, the natural seawater (pH=8), filtered (0.45 μm) and supplied by the Maritime Museum of Cantabria, was acidified by a pH controller (AT Control System). This system monitors the pH and controls the CO_2 bubbling from a CO_2 gas supply via an automated feedback relay system. Using this method, it was possible to supply large quantities of CO_2-acidified seawater with a constant pH (precision of ±0.1 pH units).

A Crison pHmeter GLP 22 with electrode, accurate to 0.01 pH units was used for pH measurement of all leachates. DOC analysis was performed following the standard UNE-EN 1484, developed by the Spanish Association for Standardisation and Certification (AENOR), with a total organic carbon Schimadzu TOC-V Analyzer, applying the difference method (Total Organic Carbon (TOC)= Total Carbon (TC)-Total Inorganic Carbon (TIC)). Cation analyses were carried out in triplicate using an Agilent 7500 ce ICP-MS and ICP-OES Perkin Elmer Optima 3200 RL. A rhodium (Rh) internal standard was applied to the samples for the ICP-MS analyses.

2.2. Leaching tests

The metal content potentially available for leaching from the sediment was determined according to the NEN 7341 standardised availability test, involving two consecutive extractions at 10 rpm with deionised water acidified by nitric acid **(**HNO_3**)** at Liquid/Solid ratios **(**L/S**)**=50 l/kg at pH=7 and at pH=4, each for 3 hours.

The CEN/T**S** 15364 acid and base neutralisation capacity (ANC/BNC) test was applied to determine the overall buffering capacity of the sediment, a key property for understanding its long-term behaviour. The methodology described in this standard test was performed using deionised water and seawater. According to the standard, the leaching agent (deionised water or seawater) with predetermined amounts of acid (HNO_3) or base (NaOH) was added to the sediment in three stages (t_0, $t_{0+30min}$, t_{0+2h}) after checking the pH value. The mixture, L/S=10 l/kg, was shaken at 10 rpm for 48 hours. The condition of equilibrium was verified and, according to the standard, eight final pH values between 4 and 12 were covered. In this case, the whole pH range was studied and the time of the experiment in the case of using seawater increased to 96 hours.

EN 12457 equilibrium leaching tests at L/S=2, 4, 10, 15, 20, 30 and 40 l/kg were performed to assess the release mechanisms of the different elements studied. This test was carried out using deionised water, natural seawater and seawater acidified at pH 7, 6 and 5 as leaching agents. Final leachates were filtered through a 0.45 μm pore size nitrocellulose filtration membrane and DOC, As, Cd, Cr, Cu, Ni, Pb and Zn concentrations were analysed [11].

The column leaching test was applied according to CEN/TS 14405, with modification of the column dimensions, to evaluate the release of the constituents as a function of time. The columns used are 15 cm diameter and 4 cm filling height, fitted with nylon filters at the bottom and the top. This column test was carried out with 1000 g of sediment placed in the column and deionised water, natural seawater and acidified seawater at pH 7, 6 and 5 as leaching agents. The up-flow rate through the columns, in experiments of 1-56 hours, was 15±2 cm/day, as is standard. Leachates at different L/S ratios, between 0.1 and 10 l/kg, were filtered through a 0.45 μm pore size

nitrocellulose filtration membrane and divided into subsamples to measure DOC, As, Cd, Cr, Cu, Ni, Pb and Zn concentrations [24].

The CEN/TS 14429 pH dependence test, with the same laboratory procedure as the acid/base neutralisation capacity test, aims to assess the concentration of contaminants after the 48 hours of the experiment. The test was carried out using deionised water and seawater as leaching agents. Leachates at 48 hours were filtered through a 0.45 µm pore size nitrocellulose filtration membrane and divided into subsamples for measuring DOC, As, Cd, Cr, Cu, Ni, Pb and Zn concentrations. The easily accessible software Visual MINTEQ (ver. 2.61) was used to model metal behaviour with pH in order to predict metal release from sediment in acidified environments [25].

3. Results

The availability test (NEN 7341) makes it possible to check the amount of each metal which may be mobilised in acidified environments. The highest difference between total concentration in sediment and availability corresponds to Cd, with a difference of three orders of magnitude. The most mobile elements are As, Ni and Zn since their difference is only one order of magnitude.

In figure 1, where the addition of acid is the positive scale and the addition of base the negative value, the titration curves (pH *vs* eq/kg) from the acid/base neutralisation capacity test using deionised water and seawater as leaching agents are shown. A high acid neutralisation capacity is obtained in both cases ($ANC_{pH=4}$=3.58 eq/kg for deionised water and $ANC_{pH=4}$=3.97 eq/kg for seawater). The major and significant differences between them are at pH values from 8 to 12; in this range differences are up to 1.5 units of pH when adding 0.15 eq/kg of base. Another relevant aspect is that when using deionised water, the maximum pH achieved was lower than 13, even by the addition of more than 6 eq/kg. Less than 4 eq/kg of base are needed to achieve pH values around 14 (Fig. 1.a) using seawater as a leaching solution.

From the titration curves at 48 and 96 hours when using seawater as a leaching agent (Fig. 1. b), the results show that in the basic pH range of 9-11, the pH values obtained at 48 hours are a little bit higher than the ones obtained after 96 hours, except for the last point (-2.5 eq/kg). In the acid zone with pH values between 4 and 7, the situation is the opposite. Thus, the use of the leaching test at longer times neutralises the pH value due to the buffer capacity of the sediment-seawater mixture, obtaining a linear pH evolution as a function of time. The two studied variables in the leaching test, type of water and contact time (Fig.1), highlight the viability of the neutralisation leaching test by the application of more realistic conditions (use of seawater at high contact time) in scenarios of potential CO_2 leakages.

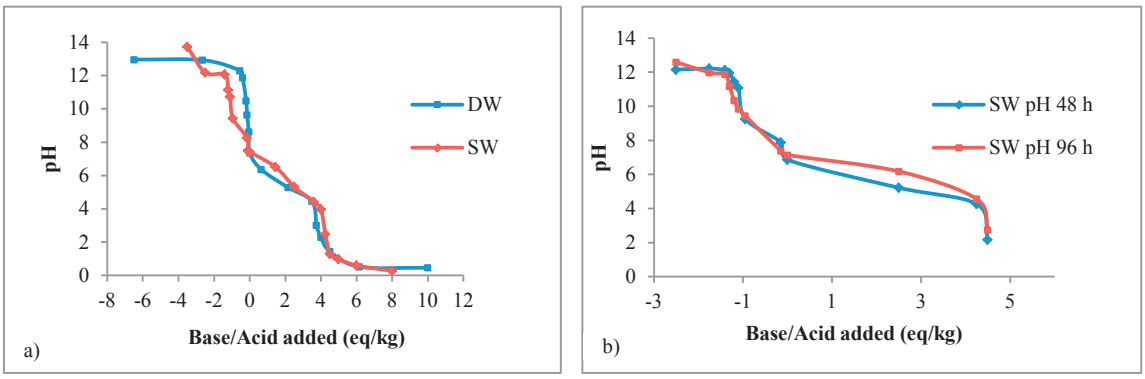

Fig. 1. a) Titration curves at 48 hours using deionised water (DW) and seawater (SW) as leaching agents; b) Titration curves at 48 and 96 hours using seawater.

According to the batch leaching test (EN 12457), release of the different inorganic species when represented as a function of L/S ratio may be solubility or availability (diffusion) controlled [26]. Thus, the effect of the change of L/S ratio gives an indication of whether solubility or availability leaching prevails. If the concentrations in the leachate (mg/l) are relatively independent of L/S ratio while the release (mg/kg) increases with L/S, it is a solubility-control mechanism. This occurs when availability is high and there is no depletion of the solid phase during the test. On the other hand, availability control results in an independent release (mg/kg) of the L/S ratio and the concentrations in the leachate (mg/l) are inversely proportional to L/S; it is typical when the leaching constituent has limited availability, and solubility is high. However, frequently there is not a clear release control mechanism and a mixture of them dominates [27, 28]. Only Cd, Ni and Zn show a clear release control mechanism at specific pH values and different leaching agents. The availability control mechanism is shown by Cd with seawater at pH values 6, 7 and 8 and by Zn with seawater at pH 6; the solubility control mechanism appears for Ni using natural seawater (pH=8) [11].

The value of the pH column leachate following the CEN/TS 14405 test is a function of time (or L/S) because it depends on the feed of the H_3O^+ ions present in the acidified seawater. Using seawater at pH 6, 7 and 8, the final leaching solution pH after 56 hours (L/S=10) is 7.6±0.07 in all cases due to the buffer capacity of the seawater. At initial pH=5, the pH is stabilised at 6.8 after approximately 11 hours (L/S=2). The DOC and metal experimental data were fitted with L/S by a potential and a linear equation respectively; the behaviour of DOC and metals with pH could be fitted by exponential equations; and the behaviour of DOC and metals with both variables at the same time (pH and L/S) by potential ones. The correlation coefficients range from 0.90 to 0.99, except for the DOC release fitted by an exponential equation, where they are from 0.80 to 0.99.

Using the pH dependence test CEN/TS 14429, the metal and organic matter release at different pH values is assessed. A DOC increase is noticeable from pH=8, with values in the pH range 0-2 slightly higher than in the neutral zone. In relation to metal release, variation of pH over 0 to 14 results in large changes in release concentrations from one (Cu) to four (Pb and Zn) orders of magnitude. Similar behaviour of DOC and metals is observed using deionised water (Fig. 2. a) and seawater (Fig. 2. b) as leaching agents. The evaluation of pH dependence of leaching is an important tool in the assessment of the expected long-term leaching behaviour of materials in different scenarios of utilisation or disposal [29], as well as in extreme and/or incidental chemical spill scenarios. The acidification bands (Fig. 2) are useful to highlight the different environments mimicked by the test: the green band represents natural seawater (pH=7.9-8), the yellow band, global ocean acidification (7.2-7.5), the orange band, acidification by leakages from a CO_2 storage site (5-7.9) [30, 31].

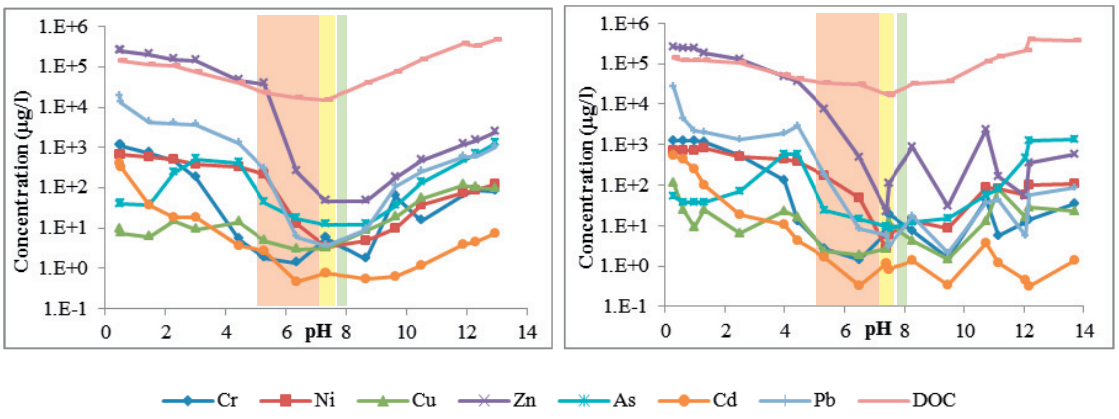

Fig. 2. pH behaviour of the studied pollutants in the CEN/TS 14429 using a) deionised water and b) seawater as leaching agents.

As shown in previous tests, different groups of metals can be distinguished. Arsenic behaves as an oxyanionic element, its release increases with the pH of the leaching solution. Amphoteric and cationic elements, Cd, Cr, Ni,

Pb and Zn, present the highest release at the lowest pH values. Cu release depends on the release of DOC, because it is a highly DOC-dependent element.

Once the experimental results were obtained and fitted to different empirical equations, the software Visual MINTEQ was used to predict metal release from sediment through the geochemical modelling. It was made considering the influence of the Fe- and Al-(hydr)oxides (HFO), humic acids (HA) and fulvic acids (FA) to improve the previous model [24] which only took into account the DOC. Thus, the differences between experimental and predicted data decreased from one-three orders of magnitude, depending on the metal, to minor differences in the acidification range of interest, from zero to one order of magnitude for most cases. In Fig. 3 the experimental and modelled results for Pb and Zn are shown. For both metals, the modelled results remain almost constant at increasing pH values from 3 to 5 while the experimental ones decrease. This is more noticeable in the case of Zn than for Pb.

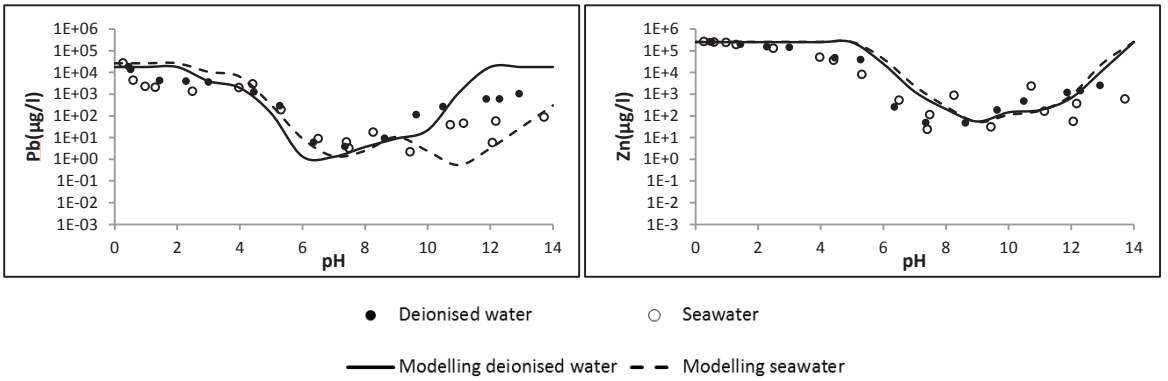

Fig. 3. Experimental (dots) and modelled (lines) results of metal leaching as a function of pH for the CEN/TS 14429 using the Visual MINTEQ geochemical model with specific organic matter influence.

4. Conclusions

Different leaching tests are used to simulate various possible scenarios of seawater acidification, including CO_2 leakages from storage sites. It is observed that the pH value of the leachates tends to neutralise at longer times due to the buffer capacity of the sediment and seawater. In any of the leaching tests used, Cd, Cr, Ni, Pb and Zn behave as cationic and amphoteric metals, being more soluble at low pH values. As has an oxyanionic behaviour whereas Cu presents a similar behaviour to DOC (Dissolved Organic Carbon). Only Cd, Ni and Zn present availability or solubility control at specific pH values and leaching agents.

Modelling with Visual MINTEQ makes it possible to predict metal release from sediment to the leaching agent in the whole pH range. Taking into account the DOC and other specific characteristics of the sediment like specific organic compounds such as humic acids and fulvic acids, differences between modelled and experimental results are from zero to one order of magnitude in the acidification range of interest (pH:5-8).

The results obtained from the different leaching tests, which simulate several scenarios of acidification, complement each other. The results allow the assessment of metal release from sediment under CO_2 acidified seawater leakages from CCS, an important issue to the implementation of this technology.

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